

# Reaction of Germanium Tetrachloride with Chloro(phenyl)silanes in the Presence of Aluminum Chloride

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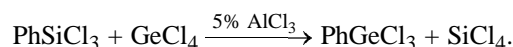
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**Abstract**—The effect of the quantity of aluminum chloride on the direction and depth of reaction of germanium tetrachloride with chloro(phenyl)silanes of the general formula  $\text{Ph}_n\text{SiCl}_{4-n}$  ( $n = 1-3$ ) was studied to show that radical exchange between germanium and silicon is initiated only if the mixture contains no less than 2.5–5 wt% of aluminum chloride. With trichloro(phenyl)silane, the radical exchange is initiated at 5 wt% of aluminum chloride and results in exclusive formation of trichloro(phenyl)germane. The reactions of  $\text{GeCl}_4$  with dichlorodiphenylsilane and chlorotriphenylsilane in the presence of 2.5–7.5 wt% of aluminum chloride give dichlorodiphenylgermane as the major product, and at  $\text{AlCl}_3$  concentrations of above 10 wt% the major product becomes to be trichloro(phenyl)germane.

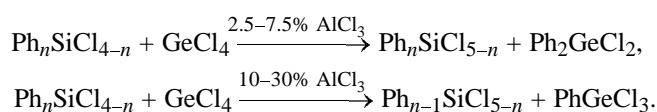
We previously observed exchange of phenyl radicals for chlorine in a mixture of dichloro(methyl)-(phenyl)silane and germanium chloride, heated in the presence of 30–40 wt% of aluminum chloride [1]. More recently this reaction was studied in detail on an example of chloro(methyl)(phenyl)silanes [2, 3], but, like in [1], it was performed in the presence of 30–40 wt% of aluminum chloride. Proceeding with this research, we studied in the present work the effect of the quantity of aluminum chloride on the direction and depth of reaction of germanium tetrachloride with chloro(phenyl)silanes  $\text{Ph}_n\text{SiCl}_{4-n}$  ( $n = 1-3$ ), as well as the possibility of radical exchange not only in the presence aluminum chloride, but also in the presence of other metal halides possessing Lewis acid properties (Table 1).

It was found that no reaction occurred in the presence of antimony trichloride, tin tetrachloride, or titanium tetrachloride, whereas the reaction with chloro(phenyl)silanes in the presence of boron trifluoride etherate gave fluoro(phenyl)silanes.

At the same time, chlorine at germanium in  $\text{GeCl}_4$  exchanged for phenyl at silicon as the concentration of  $\text{AlCl}_3$  was decreased to 5 wt% in the reaction with trichloro(phenyl)silane and to 2.5 wt% in the reactions with dichloro(phenyl)- and chlorotriphenylsilanes. The reaction with trichloro(phenyl)silane resulted in exclusive formation of trichloro(phenyl)germane.



The reactions of  $\text{GeCl}_4$  with dichlorodiphenylsilane and chlorotriphenylsilane in the presence of 2.5–7.5 wt% of aluminum chloride afforded dichlorodiphenylgermane as the major product, while at  $\text{AlCl}_3$  concentrations of above 10 wt% the major product became to be trichloro(phenyl)germane.



Obviously, as the fraction of aluminum chloride in the reaction mixture is increased, dichloro(diphenyl)-

**Table 1.** Reaction of  $\text{Ph}_2\text{SiCl}_2$  with  $\text{GeCl}_4$  (1:1) in the presence of various metal halides

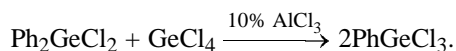
Catalyst (%)	T, °C	Composition of the reaction mixture, %			
		$\text{PhSiCl}_3$	$\text{Ph}_2\text{SiCl}_2$	$\text{Ph}_2\text{SiF}_2$	$\text{GeCl}_4$
$\text{SbCl}_3$ (30)	100–110	4.1	51.2	–	44.6
$\text{SbCl}_3$ (50)	125–135	14.7	46.6	–	38.7
$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (50)	125–135	–	–	15.0	38.7
$\text{TiCl}_4$ (50)	135	No reaction			

**Table 2.** Reaction of  $\text{Ph}_n\text{SiCl}_{4-n}$  with  $\text{GeCl}_4$  in the presence of  $\text{AlCl}_3$ 

$\text{Ph}_n\text{SiCl}_{4-n}$	$\text{Ph}_n\text{SiCl}_{4-n}:\text{GeCl}_4$ ratio	Catalyst (%)	$T, ^\circ\text{C}$	Composition of the reaction mixture, %						
				$\text{PhSiCl}_3$	$\text{Ph}_2\text{SiCl}_2$	$\text{Ph}_3\text{SiCl}$	$\text{PhGeCl}_3$	$\text{Ph}_2\text{GeCl}_2$	$\text{GeCl}_4$	$\text{SiCl}_4$
$\text{PhSiCl}_3$	1:1	$\text{AlCl}_3$ (2.5)	115–125	No reaction						
$\text{PhSiCl}_3$	1:1	$\text{AlCl}_3$ (5)	115–125	45.2	–	–	2.8	–	46.3	5.7
$\text{PhSiCl}_3$	1:1	$\text{AlCl}_3$ (7.5)	115–125	39.8	–	–	4.9	–	44.9	10.4
$\text{PhSiCl}_3$	1:1	$\text{AlCl}_3$ (10)	115–125	40.4	–	–	46.1	–	8.9	4.5
$\text{PhSiCl}_3$	1:1	$\text{AlCl}_3$ (20)	115–125	16.9	–	–	49.8	–	27.9	5.4
$\text{PhSiCl}_3$	2:1	$\text{AlCl}_3$ (10)	145	49.3	–	–	38.3	–	7.5	4.9
$\text{PhSiCl}_3$	2:1	$\text{AlCl}_3$ (15)	150	47.1	–	–	36.5	–	10.9	3.5
$\text{PhSiCl}_3$	2:1	$\text{AlCl}_3$ (20)	155	36.1	–	–	28.5	–	32.6	2.9
$\text{Ph}_2\text{SiCl}_2$	1:1	$\text{AlCl}_3$ (2.5)	150	54.0	1.0	–	9.0	16.0	0.2	19.7
$\text{Ph}_2\text{SiCl}_2$	2:1	$\text{AlCl}_3$ (2.5)	130–135	44.3	19.3	–	0.2	22.5	13.7	–
$\text{Ph}_2\text{SiCl}_2$	1:1	$\text{AlCl}_3$ (3.5)	150	51.8	0.1	–	25.5	2.8	0.9	18.1
$\text{Ph}_2\text{SiCl}_2$	1:1	$\text{AlCl}_3$ (5)	135–145	29.9	1.1	–	40.4	4.7	16.7	6.3
$\text{Ph}_2\text{GeCl}_2$	1.35:1	$\text{AlCl}_3$ (5)	70–80	–	–	–	23.2	20.1	55.8	–
$\text{Ph}_2\text{SiCl}_2$	2:1	$\text{AlCl}_3$ (5)	110	58.9	1.8	–	4.8	27.6	–	6.3
$\text{Ph}_2\text{SiCl}_2$	1:1	$\text{AlCl}_3$ (10)	120–150	41.7	0.5	–	43.2	2.8	0.8	10.9
$\text{Ph}_2\text{GeCl}_2$	1.35:1	$\text{AlCl}_3$ (10)	100	–	–	–	73.4	–	–	–
$\text{Ph}_2\text{SiCl}_2$	1:1	$\text{AlCl}_3$ (20)	110	17.3	0.3	–	49.1	–	27.9	5.5
$\text{Ph}_3\text{SiCl}$	1:1	$\text{AlCl}_3$ (2.5)	150	No reaction						
$\text{Ph}_3\text{SiCl}$	1:1	$\text{AlCl}_3$ (5)	145	–	5.4	80.1	–	–	14.5	–
$\text{Ph}_3\text{SiCl}$	1:1	$\text{AlCl}_3$ (5)	150–155	1.6	35.5	49.3	–	0.8	12.8	–
$\text{Ph}_3\text{SiCl}$	1:1	$\text{AlCl}_3$ (7.5)	140	26.7	25.4	2.0	–	37.6	3.8	2.8
$\text{Ph}_3\text{SiCl}$	Excess $\text{GeCl}_4$ (1:1.5)	$\text{AlCl}_3$ (7.5)	145	37.9	–	–	11.5	46.4	1.0	2.1
$\text{Ph}_3\text{SiCl}$	1:1	$\text{AlCl}_3$ (10)	135	53.8	–	1.2	17.6	26.6	0.8	–
$\text{Ph}_3\text{SiCl}$	2:1	$\text{AlCl}_3$ (10)	135	13.5	54.9	7.5	–	18.2	4.8	–
$\text{Ph}_3\text{SiCl}$	3:1	$\text{AlCl}_3$ (10)	150–155	15.5	53.9	13.8	–	14.9	–	–
$\text{Ph}_3\text{SiCl}$	1:1	$\text{AlCl}_3$ (20)	125	67.3	–	–	28.7	0.5	–	–
$\text{Ph}_3\text{SiCl}$	1:1	$\text{AlCl}_3$ (30)	135	52.6	–	–	40.0	1.9	4.7	0.7
$\text{Ph}_3\text{SiCl}$	No $\text{GeCl}_4$ added	$\text{AlCl}_3$ (7.5)	140–145	–	29.8	70.2	–	–	–	–
$\text{Ph}_3\text{SiCl}^a$	With $\text{GeCl}_4$ added (1:1)	$\text{AlCl}_3$ (7.5)	140	39.2	–	0.3	8.6	47.1	2.4	0.9

<sup>a</sup>  $\text{GeCl}_4$  was added to preliminarily heated mixture of  $\text{Ph}_3\text{SiCl}$  with  $\text{AlCl}_3$ .

germane enter reaction with unreacted germanium tetrachloride to form trichloro(phenyl)germane. Evidence for this suggestion was obtained in a special experiment (Table 2).



## EXPERIMENTAL

All experiments were performed with commercial reagents.

Reaction products were analyzed by GLC on an LKhM-80 chromatograph: metallic column 1000.3 mm,

packing 5% SE-30 on Chromasorb G-AW-DMCS (0.15–0.18 mm); the oven temperature was programmed from 50 to 290°C at a rate of 12 deg min<sup>–1</sup>. Injector temperature 320°C, thermal conductivity detector, detector temperature 300°C, detector current 90 mA. Carrier gas helium, rate 30 ml min<sup>–1</sup>.

**Reaction of chloro(phenyl)silanes with tetrachlorogermane.** A mixture of chloro(phenyl)silane, tetrachlorogermane, and aluminum chloride was heated at 100°C for 3 h and then cooled and analyzed by GLC. The calculated product yields are given in Tables 1 and 2.

## REFERENCES

1. Chernyshev, E.A., Kurek, M.E., and Polivanov, A.N., USSR Inventor's Certificate no. 316693, 1970, *Byull. Izobret.*, 1971, no. 30.
2. Motsarev, G.V., Chernyshev, E.A., Rozenberg, V.R., Inshakova, V.T., and Zetkin, V.I., *Zh. Obshch. Khim.*, 1983, vol. 53, no. 5, p. 1111.
3. Lakhtin, V.G., Yakovleva, M.V., and Chernyshev, E.A., Available from VINITI, 2002, Moscow, no. 2071-V2002.